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(71) Applicant: THE DOW CHEMICAL COMPANY, 2030 Dow Center Abbott Road P.O. Box 1967, Midland, MI 48640 (US)

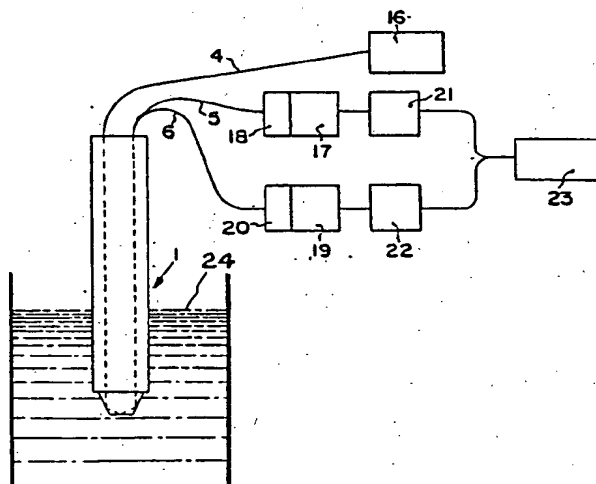
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Bulletin 86/52(72) Inventor: McLachlan, Richard D., 2412 Damman Street, Midland Michigan 48640 (US)
Inventor: Chrisman, Ray W., 5501 Swede Road, Midland Michigan 48640 (US)

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(74) Representative: Smulders, Theodorus A.H.J. et al, Vereenigde Octroolbureaux Nieuwe Parklaan 107, NL-2587 BP 's-Gravenhage (NL)

(54) Methods and apparatus for measuring the light absorbance of a fluid medium.

(57) The presence and concentration of a light absorbing constituent in a fluid medium is determined in-situ by immersing in such medium a probe having a prism at one end and whose refractive index is greater than that of the medium and causing light including a wavelength absorbable by such constituent to traverse an optical path through the prism and undergo successive attenuated total reflections. At each reflection some of the light will be absorbed by the constituent. The intensity of light emerging from the prism is measured at one or more wavelengths, including one absorbable by such constituent. The concentration of the constituent is determined by comparison of the measured intensity with values obtained from like measurements performed on like mediums containing known concentrations of the constituent.



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METHODS AND APPARATUS FOR MEASURING
THE LIGHT ABSORBANCE OF A FLUID MEDIUM

This invention relates to the measurement of concentrations of light absorbing constituents of fluid mediums. It is particularly useful for in-situ analyses of mediums having high absorbance
5 characteristics.

Absorption spectroscopy in the ultraviolet (UV) wavelength range is a widely used method for analysis of organic materials which absorb UV
10 radiation. Due to the high absorptivities (i.e., large extinction coefficients) of UV absorbing compounds, absorption measurements customarily are performed on samples diluted with UV transparent solvents. Dilution factors of 100 to 10,000
15 commonly are employed in conjunction with absorption cells having pathlengths of from 1 mm to 10 cm. Absorption measurements of undiluted samples would require the use of cells with pathlengths on the order of 1 micrometer. The necessity of either
20 diluting the sample or employing absorption cells of

inconveniently short pathlengths has severely limited the application of UV absorption spectroscopy for in-situ analyses in chemical processes.

5 The concentrations of light absorbing constituents of a fluid medium are determined by the use of a fiber optic probe having two groups of optical fibers optically coupled to a transparent prism whose refractive index exceeds that of the
10 medium to be analyzed. One group of fibers is used to transmit light to a prism having a wavelength that can be absorbed by a particular constituent of the fluid medium. The prism has at least two angularly displaced, adjacent faces in contact with
15 the medium. Within the prism the light undergoes successive attenuated total internal reflections and emerges from the prism via the second group of optical fibers which transmit the reflected light outwardly of the probe to an apparatus which
20 measures the intensities of the reflected light at one or more wavelengths. The measured values of the intensities thus obtained are compared with corresponding values obtained in the same way using like mediums, but containing known concentrations of
25 the constituent, thereby enabling the concentration

of the absorbing constituent in the medium under analysis to be determined.

Figure 1 is a fragmentary, vertical sectional view taken on line 1-1 of Figure 2 and illustrating a probe according to one embodiment of the invention;

Figure 2 is a top plan view of the probe shown in Figure 1;

Figure 3 is a diagrammatic view similar to Figure 1, but illustrating a second embodiment;

Figure 4 is a view similar to Figure 2, but illustrating a further embodiment;

Figures 5 and 6 are diagrammatic views illustrating other forms of prisms which may be used with the probes;

Figure 7 is a diagrammatic view illustrating apparatus required for performing the process according to one embodiment; and

Figure 8 is a view similar to Figure 7, but illustrating a modified embodiment of the apparatus.

The invention is predicated on the concept that, when light traveling within a medium impinges upon a boundary between that medium and a medium of lower refractive index, it either passes into the second medium or is totally internally reflected,

depending on whether the quantity $\frac{n}{n'} \sin I$ (where n and n' are the refractive indices of the first and second mediums, respectively, and I is the angle of incidence) is less than or greater than one. If

5 $\frac{n}{n'} \sin I$ is greater than one, total internal reflection occurs. Although the internal reflection is referred to as a total, the light, during the reflection process, penetrates a short distance into the second medium. The depth of penetration depends

10 in a complex and known manner on the refractive indices of the two mediums and the angle of incidence, but usually is on the order of tenths of the wavelength of the light. If the incident light includes a wavelength absorbed by a constituent of

15 the second medium, light of such wavelength will be partially absorbed or attenuated during reflection due to the penetration of the light into the second medium.

This effect is called attenuated total reflection

20 (ATR). Due to the very shallow penetration of the light into the second medium, ATR is a useful technique for measuring absorbance by strongly absorbing materials.

The requirement that the refractive index of

25 the prism exceed that of the medium limits the

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choice of prism materials. For use in the mid-ultraviolet region (200-300 nm wavelengths), only silica ($n = 1.51$ at 250 nm), sapphire ($n = 1.84$ at 250 nm), and diamond ($n = 2.7$ at 250 nm) have sufficiently high refractive indices and transmissions to be useful. Silica is useful only for samples of relatively low refractive index, such as aqueous solutions. Diamond is very expensive and does not transmit wavelengths below 225 nm. Thus, sapphire is the most useful material for ATR measurements in the UV range.

In-situ ATR measurements conveniently can be made according to the invention by the use of a probe having a hollow housing formed of material that can be immersed in a fluid medium containing a constituent capable of absorbing light of a specific wavelength. Light of preferably substantially constant intensity is conducted from a source remote from the medium via one or more optical fibers to one end of the probe. At the other end of the probe is a prism having a plurality of angularly displaced, adjacent faces in contact with the medium. Light transmitted to the probe is totally internally reflected from the first face of the prism to each other face thereof in succession and from the last face to one or more optical fibers

which conduct the reflected light out of the probe to an apparatus for measuring its intensity. Each time the light is reflected within the prism, the absorbing constituent in the medium will absorb some
5 of the light, thereby reducing its intensity. The intensity of light transmitted by the probe at wavelengths absorbed by a constituent thus is inversely related to the concentration of that constituent.

10 The apparatus may be calibrated by immersing the probe in two or more calibrating mediums and measuring in each case the intensity of the transmitted light at a wavelength absorbed by a particular constituent in each medium. The
15 calibrating mediums correspond to that to be analyzed, but contain known concentrations of the light absorbing constituent. The apparatus then may be used in a like manner to measure the intensity of transmitted light following immersion of the probe
20 in a like medium containing a like constituent of unknown concentration. The intensities obtained from the calibrating mediums and the medium under analysis may be compared to obtain the concentration of the absorbing constituent in the latter medium.
25 The effective path of the light in a medium being analyzed is approximately proportional to

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$N/\cos I$, where N is the number of reflections and I is the angle of incidence. The upper limit of the refractive index (n') of the fluid medium is given by the formula $n' = n \sin I$, where n is the

5 refractive index of the prism material. Since the choice of the prism materials is limited, it is convenient to vary the angle of incidence and/or the number of reflections to accommodate samples of various refractive indices and absorbtivities.

10 A probe 1 according to the embodiment of Figure 1 has a hollow body 2 formed of metal or other material suitable for immersion in a chemical process fluid that is to be analyzed. Each end of the body is closed except for openings 3 which
15 accommodate known clad optical fibers. In this embodiment there are three fibers 4, 5, and 6, respectively, fixed in the openings 3, but there can be as few as two such fibers diametrically opposite one another. At one end of the body is an external
20 groove 7 which accommodates a sealing ring 8 that encircles the openings 3. Seated on the sealing ring is a trapezoidal prism 9 formed of a high refractive index material, such as sapphire. Between the prism and the confronting ends of the
25 optical fibers is an optical coupling gel or oil 9a. A clamp 10 maintains the prism in place at the

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end of the probe and is secured to the body screws
11. The prism has a flat base 12 and three external
faces 13, 14, and 15.

To condition the apparatus thus far described
5 for use, one of the optical fibers that extends from
the probe body 2 is coupled to a substantially
constant intensity light source 16 that is remote
from the probe. The light source may be a deuterium
lamp if light in the UV range is to be used. As
10 shown in Figure 7 the fiber 4 is coupled to the
light source and such fiber hereinafter will be
referred to as the input fiber. The other two
fibers 5 and 6 shown in Figures 2 and 7 will be
referred to hereinafter as output fibers.

15 The output fiber 5 is optically coupled to a
silicon diode detector 17 via a bandpass filter 18
and the output fiber 6 also is coupled to a similar
detector 19 via a bandpass filter 20. The filters
isolate two discrete, different wavelengths. The
20 outputs from the detectors 17 and 19 are amplified
by trans-impedance amplifiers 21 and 22, respec-
tively, and transmitted to a computer 23 which
measures the intensities of the respective
wavelengths and computes the concentration of the
25 associated constituent.

In the embodiment shown in Figures 1, 2, and 7,

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that end of the probe 1 from which the prism 9 projects is immersed in a fluid medium 24 containing a constituent that will absorb light of a particular wavelength. The light emitted by the source 16, 5 includes the particular wavelength absorbable by the constituent and is conducted by the input fiber 4 to the base 12 of the prism 9 along a path that is normal to the base. Light enters the prism and is transmitted along a path 25 which impinges on the 10 face 13 at an angle of incidence which effects total internal reflection of the light along a path 26 to the face 14 where total internal reflection again occurs to cause the light to travel along a path 27 to the face 15 where once again the light is totally 15 reflected along a path 28 toward the prism base 12. Light emitted from the input fiber diverges as it traverses the optical path through the prism. The overall length of such optical path is so selected as to illuminate both of the output fibers 5 and 6 20 from the single input fiber.

Assuming that the filter 18 transmits light of a wavelength not absorbed by any constituent of the medium, then the signal from the detector 17 constitutes a calibration signal. If the filter 20 25 transmits light of a frequency absorbed by the constituent, then the signal from the detector 19

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will vary inversely with the concentration of the absorbing constituent. The ratio of the respective signals, as determined by the computer, enables the concentration of the absorbing constituent to be
5 determined.

It is not necessary that two output fibers be used; one is sufficient. However, the use of two output fibers enables the calibration and the concentration procedures to be conducted
10 simultaneously, whereas if a single output fiber were used the calibration would require the immersion of the probe in a medium corresponding to the medium 24, but from which the absorbing
constituent has been omitted. In this instance the
15 values of the calibrating and the other intensities have to be determined sequentially and then compared.

For the process according to the invention to function reliably, it is necessary that each output fiber be illuminated fully. It is desirable to
20 minimize the length of the optical path in the prism because of the divergence of the transmitted light and the consequent reduction of its intensity.

It is not necessary that the probe be limited to a single input fiber or to one or two output
25 fibers. Figure 4 illustrates a probe having three input fibers 24a and three output fibers 25a. Light

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emitted from each of the input fibers will illuminate more than one of the output fibers. Thus, a construction having three input fibers and three output fibers may transmit as much as four to
5 eight times as much light as a two-fiber probe and enable the analysis of the concentrations of multiple constituents simultaneously.

Figure 3 illustrates an embodiment of the invention which differs from the others in that the
10 input and output optical fibers 26a and 27a are inclined with respect to the probe axis by an angle of 10 to 30° and converge in a direction toward a prism 28a. The base angles are reduced appropriately. This results in an increase in the angle of
15 incidence and thus allows the probe to operate in mediums of higher refractive index.

If the refractive index of the prism shown in Figure 3 is different from that of the optical fibers, light will be refracted on entering and
20 leaving the prism. The angle x' between the axis of the optical path entering the prism and the probe axis is related to the angle x between the fiber axis and the probe axis by the relation $\sin x' = \frac{n^*}{n}$
sin x , where n^* is the refractive index of the fiber
25 and n is the refractive index of the prism. The angle of incidence is given by

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$$I = \frac{180}{3} + x' = \frac{180}{3} + \sin^{-1} \left[\frac{n^*}{n} \sin x \right].$$

A probe according to Figure 3 may include a sapphire prism and quartz fibers with an angle of 30° between the fiber axes and the probe axis. Such a probe has an angle of incidence of about 68°. It is thus useful in analyzing materials having refractive indices as high as 1.71 at 250 nm.

The number of reflections to which the transmitted light is subjected is not limited to two or three. Figure 5 shows a prism 30 having a base 31 and four faces 32, 33, 34, and 35 which produce four reflections. The angles of incidence and the base angles are 67.5°. The prism 36 of Figure 6 has a base 37 and five faces 38, 39, 40, 41, and 42 which produce five reflections. The angles of incidence and the base angles are 72°.

Probes producing four and five reflections also can be constructed with fibers that are parallel to the probe axis. Such a probe having five reflecting surfaces, and its fiber axes inclined 30° with respect to the probe axis, has angles of incidence of about 77°. Thus it is useful in samples with refractive indices up to about 1.79 at 250 nm.

Probes with larger angles of incidence and

larger numbers of reflecting surfaces could be constructed, but these would not increase significantly the range of refractive indices inasmuch as the ultimate limit is 1.84, i.e., the refractive index of the sapphire prism material.

For many applications, it is desirable to maximize the light transmissions through the prism. For maximum light transmission the optical fibers should have relatively large core diameters. Fibers with core diameters of about 0.6 mm are preferred because larger fibers are more expensive and difficult to handle due to their large bending radii. It is desirable to minimize the length of the optical path in the prism because of the divergence of the transmitted light and the consequent reduction in its intensity.

The light transmission can be increased by the use of multiple fibers to conduct light to and from the prism. Within limits imposed by the size and aperture angle of the light source, the amount of light conducted to the prism is proportional to the total surface area of the fiber ends, i.e., to the product of the cross sectional area of one fiber and the number of input fibers. Standard deuterium lamps with apertures of 1 mm can fully illuminate three fibers with core diameters of 0.6 mm and a

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numerical aperture of 0.25.

A probe according to Figure 4 could have its output fibers 25 coupled to three filter-detector systems of the kind shown in Figure 7 for measuring the transmittance at three different wavelengths, thus allowing simultaneous measurements of the concentrations of two components. Alternatively, the output fibers of any of the probes can be arranged linearly as shown in Figure 8 and coupled to a spectrophotometer 46 for scanning a spectrum. Systems can be constructed to allow analyses of samples with three or more components.

1. A probe for determining the concentration of a light absorbing constituent in a fluid medium, said probe comprising a housing immersible in said medium and terminating at one end in a prism having
5 a base and at least two adjacent, angularly displaced, externally exposed faces; at least one optical input fiber extending from adjacent said base outwardly of said housing for optical coupling to a source of light including a wavelength absorbable by said constituent;
10 and at least one optical output fiber extending from adjacent said base outwardly of said housing for optical coupling to light intensity measuring apparatus, said one end of each of said input and output fibers being so positioned relative to one another and to
15 said prism that light transmitted from said one end of said input fiber into said prism is totally internally reflected by said faces onto said one end of said output fiber.

2. The probe according to Claim 1, wherein
20 said one end of said input fiber is parallel to said one end of said output fiber.

3. The probe according to Claim 1, wherein
said one end of said input fiber and said one end of
said output fiber are arranged on lines which converge
25 in the direction of said prism.

4. An apparatus for determining the presence in a fluid medium of a light absorbing constituent, said apparatus comprising a probe having a housing; a transparent prism at one end of said housing having
5 a base and at least two adjacent, angularly displaced external faces; a source of light including a wavelength absorbable by said constituent; at least one optical input fiber supported by said probe for transmitting light from said source to the base of said prism;
10 at least one optical output fiber supported by said probe for transmitting light from said base externally of said housing; and means coupled to said output fiber for measuring the intensity of light transmitted thereby, said fibers and said faces of said prism
15 being so arranged relative to one another that light transmitted to said base by said input fiber enters said prism and is totally internally reflected by said faces onto said output fiber.

5. The apparatus according to Claim 4,
20 wherein said housing is formed of material capable of immersion in said medium.

6. The apparatus according to Claim 4,
wherein said light source emits light of at least two different wavelengths one of which is not absorbable
25 by said constituent, and wherein said apparatus includes a second output fiber adjacent a first output fiber, and a second light intensity measuring means coupled to said second output fiber for measuring the intensity of light transmitted thereby.

7. The apparatus according to Claim 4
30 including a plurality of output fibers, and a cor-

responding plurality of light intensity measuring means coupled to the respective output fibers.

8. A method for determining the concentration of at least one light absorbing constituent in a fluid medium, said method comprising:

(a) immersing in said medium a probe having at one end thereof a prism, said prism having a refractive index greater than that of said medium and having at least two angularly displaced, adjacent faces in contact with said medium;

(b) transmitting light from a source to said prism, said light including at least one wavelength absorbable by said constituent and being transmitted into the prism at such an angle of incidence relative to said faces so as to be totally internally reflected within said prism and thence outwardly of said probe through its other end;

(c) measuring the intensity of the light of said wavelength that emerges from said probe; and

(d) comparing the intensity value thus obtained to corresponding values obtained by the application of steps (a), (b), and (c) to at least two calibration mediums like said fluid medium but containing different, known concentrations of said constituent.

9. The method according to Claim 8, wherein the light transmitted into said prism enters and leaves said prism along spaced, parallel paths.

10. The method according to Claim 8, wherein the light transmitted to said prism and the light

reflected from said prism enter and leave said prism along spaced paths that converge in a direction toward said prism.

11. A method for determining the concentration of at least one light absorbing constituent in a fluid medium, said method comprising:

(a) immersing in said medium a probe having at one end thereof a prism, said prism having a refractive index greater than that of said medium and having at least two angularly displaced, adjacent faces in contact with said medium;

(b) transmitting light from a source to said prism, said light including at least one wavelength absorbable by said constituent and at least one other wavelength not absorbable by said constituent and being transmitted into said prism at such an angle of incidence so as to be totally internally reflected within said prism and thence outwardly of said probe through its other end;

(c) measuring the intensity of the reflected light of each of said wavelengths to obtain a ratio therebetween; and

(d) comparing the ratio thus obtained to corresponding ratios obtained by the application of steps (a), (b), and (c) to calibration mediums like said fluid medium but containing different, known concentrations of said constituent.

12. The method according to Claim 11, wherein said fluid medium contains a plurality of different light absorbing constituents and wherein the light transmitted to said prism includes a frequency absorbable by each of said constituents.

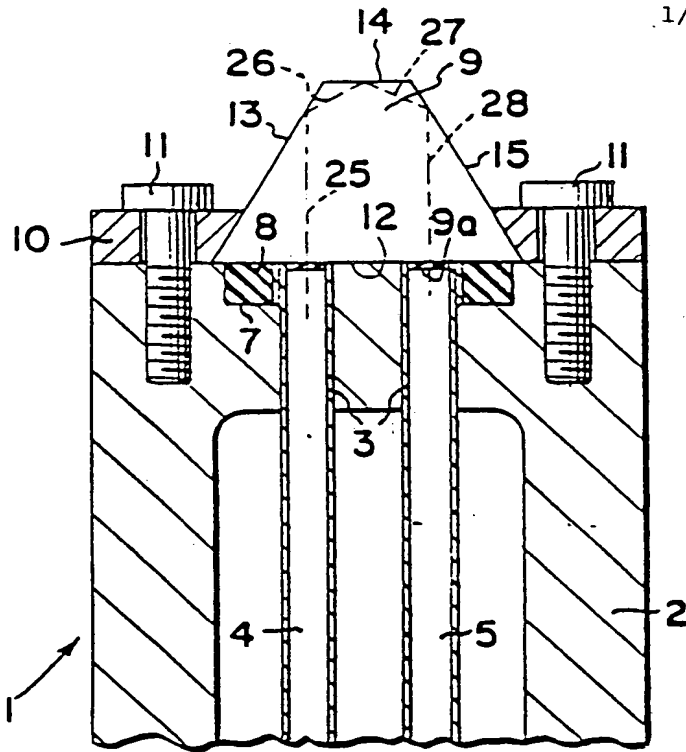


FIG. 1

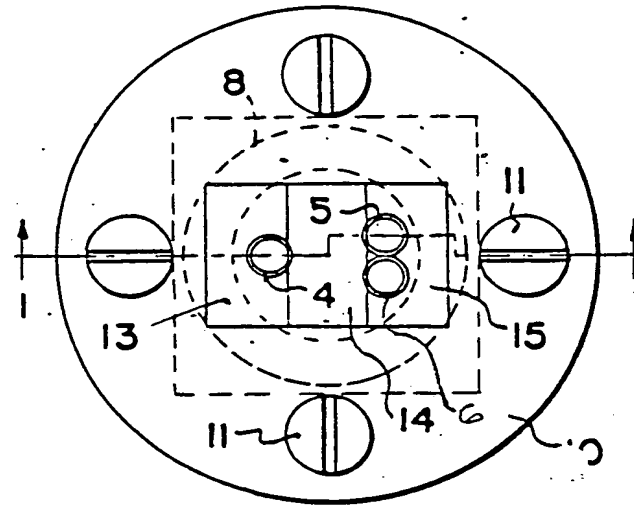


FIG. 2

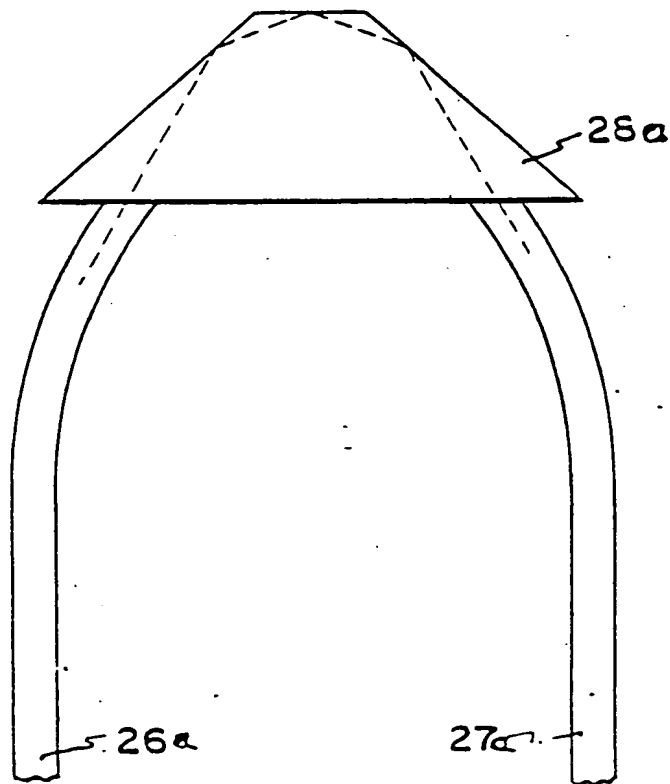


FIG. 3

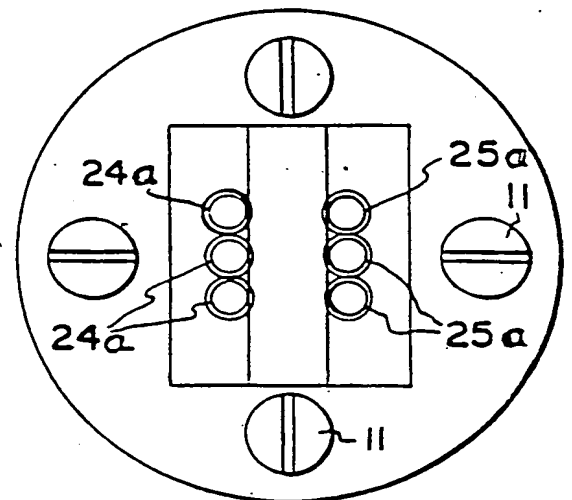


FIG. 4

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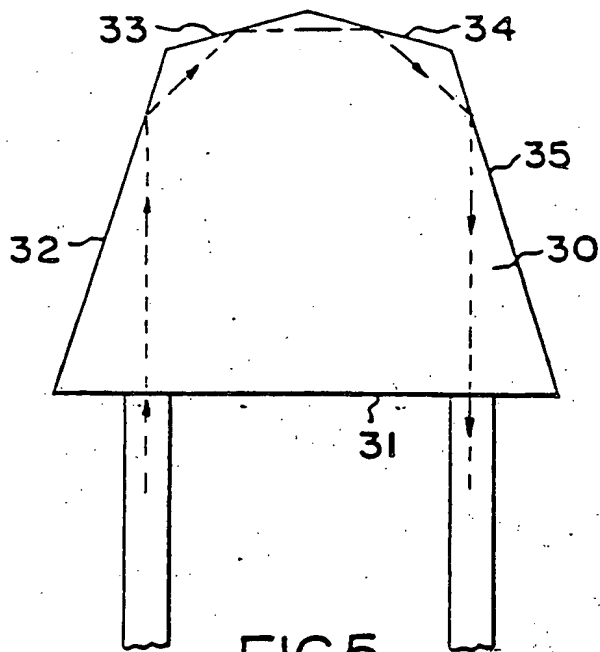


FIG. 5

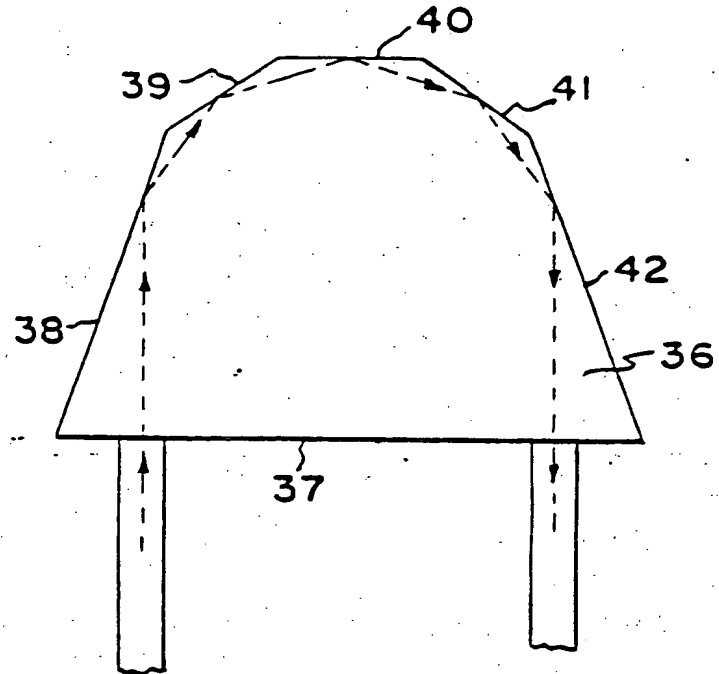


FIG. 6

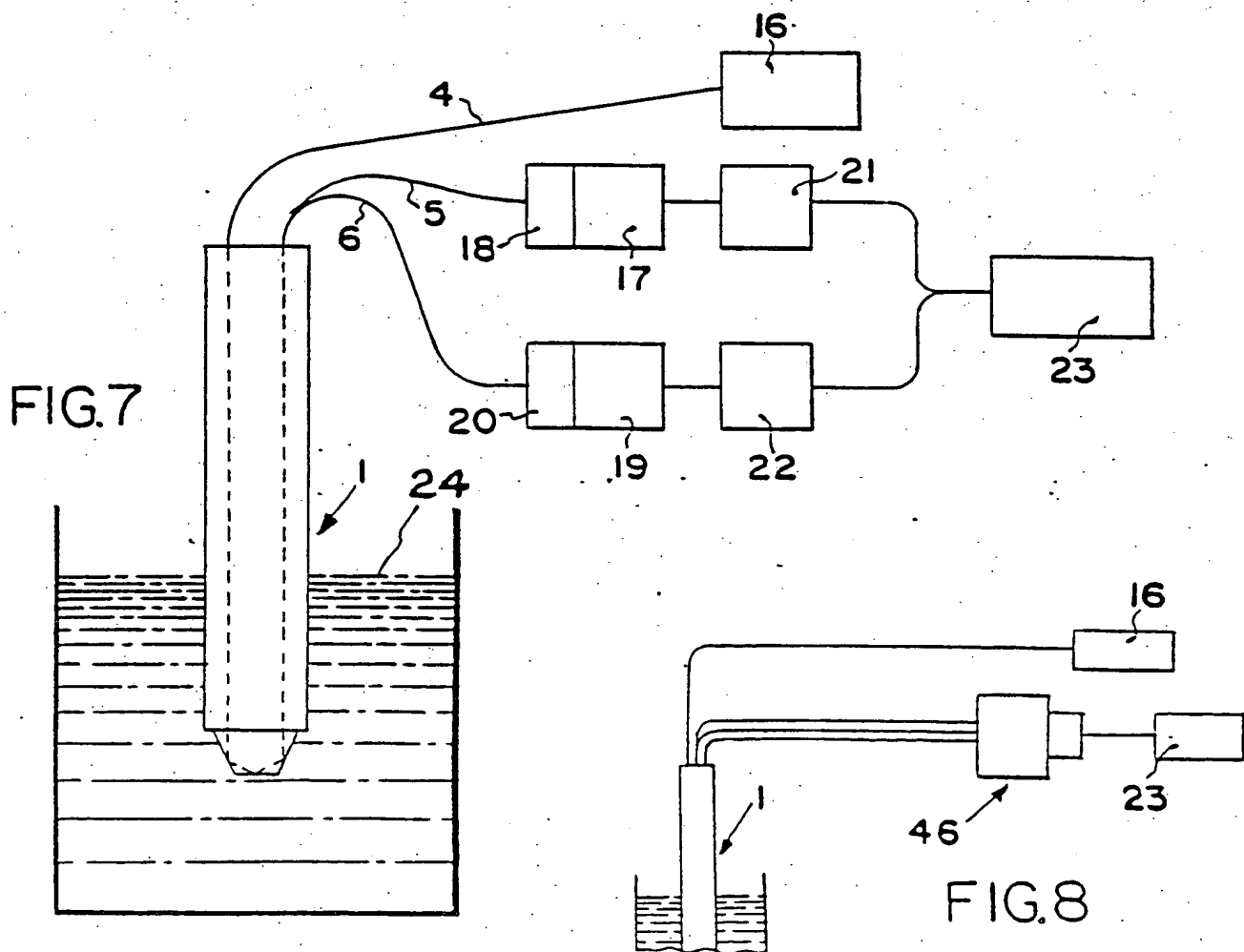


FIG. 7

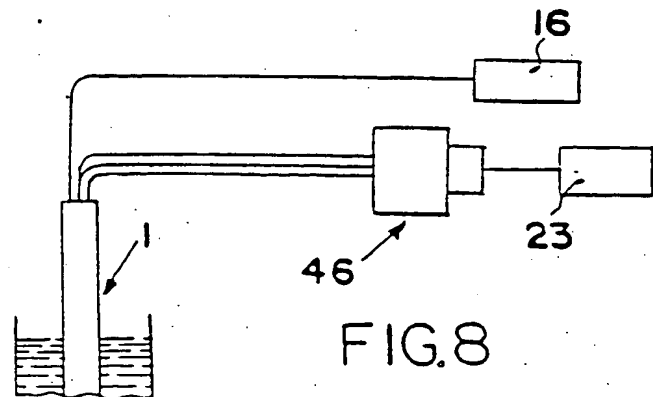


FIG. 8

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